▪CHEM 1212 - Principles of Chemistry II

Chapter 16 - Spontaneity, Entropy, and Free Energy

16.1 Spontaneous Processes and Entropy

- a process is said to be spontaneous if it occurs without outside intervention
- spontaneous processes may be fast or slow
- thermodynamics tell us the direction of the process but not the speed
- thermodynamics only considers the initial and final states and does not require knowledge of the pathway between reactants
- see Figure 16.2
- after many years of observation, scientists have concluded that the characteristic common to all spontaneous processes is an increase in a property called **entropy**, denoted by the symbol, **S**
    - the driving force for a spontaneous process is an increase in the entropy of the universe
    - entropy can be viewed as a measure of randomness or disorder
    - entropy is thermodynamic function that describes the number of arrangements (positions and/or energy levels) that are available to a system existing in a given state
- energy is closely associated with probability
    - see Figure 16.3
    - see Figure 16.4
    - see Table 16.1
    - see Table 16.2
- the type of probability we have been considering in this example is called positional probability because it depends on the number of configurations in space (positional microstates) that yield a particular state
- $S_{solid} < S_{liquid} << S_{gas}$

16.2 Entropy and the Second Law of Thermodynamics

- ***in any spontaneous process there is always an increase in the entropy of the universe - this is the second law of thermodynamics***
- energy is conserved in the universe, but entropy is not
- the second law can be paraphrased as follows; the entropy of the universe in increasing
- convenient to divide the universe into a system and the surroundings thus the change in the entropy of the universe is equal to the entropy of the system and the change in entropy of the surroundings
- if the change in the entropy of the universe is positive, the process is spontaneous in the direction written; if negative spontaneous in the opposite direction; if zero the process has no tendency to occur and the system is at equilibrium

16.3 The Effect of Temperature

- example, $H_2O(l)$ --> $H_2O(g)$; this is the system everything else the surroundings
- a mole of water has a volume of approximately 18 mL; a mole of gaseous water at 1 atm and $100^{o}C$ occupies a volume of approximately 31 liters; entropy increases in this system
- when heat is release to the surrounding (exothermic reaction), entropy of the surrounding is increased; the reverse occurs in endothermic reactions
- the sign of) S_{univ} tells us whether the vaporization of water is spontaneous or not
- have seen that) S_{sys} is positive and favors the process and) S_{surr} is negative and unfavorable; thus the components are in opposition; which controls the situation?; depends on the temperature
- at 1 atm, water changes spontaneously from liquid to gas at all temperatures above $100^{o}C$; below $100^{o}C$ the opposite process (condensation) is spontaneous
- the central idea is that the entropy changes in the surroundings are primarily determined by heat flow
- an exothermic process in the system increases the entropy of the surroundings, because the resulting energy flow increases the random motions in the surroundings; this means that exothermicity is an important driving force for spontaneity
- the significance of exothermicity as a driving force depends on the temperature at which the process occurs
- the impact of the transfer of a given quantity of energy as heat to or from the surrounding will be greater at lower temperatures
- definition of) S_{surr} is) S_{surr}= -) H/T
- the minus sign is necessary because the sign of) H is determined with respect to the reaction system, and this equation expresses a property of the surroundings; this mean if the reaction is exothermic,) H has a negative sign, but heat flows into the surroundings,) S is positive
- see Table 16.3

16.4 Free Energy

- so far have used S_{univ} to predict the spontaneity of a process; however, another thermodynamic function is also related to spontaneity and is especially useful in dealing with the temperature dependence of spontaneity; the function is called the **free energy**, which is symbolized by G and defined by $G = H - TS$; H is the enthalpy, T is the temperature in Kelvin, and S is the entropy
- for a process that occurs at constant temperature, the change in free energy () G) is given by the equation,) $G =$) $H - T$) S
- a process at constant T and P is spontaneous in the direction in which the free energy decreases; that the change in free energy must be negative
- now have two functions that can be used to predict spontaneity; the entropy of the universe, which applies to all processes; and free energy, which can be used for processes carried out at constant temperature and pressure; since so many chemical reactions occur under the latter conditions, free energy is the more useful to chemists

- see Table 16.5

16.5 Entropy Changes in Chemical Reactions

- the second law of thermodynamics says a process will be spontaneous if the entropy of the universe increases when the process occurs
- interested in predicting the sign of) S
- in thermodynamics it is the change in a certain function that is usually important
- it is fortunate that changes in thermodynamic functions are sufficient for most purposes, since absolute values for many thermodynamic characteristics of a system, such as enthalpy or free energy, cannot be determined
- however, can assign absolute entropy values
- the entropy of a perfect crystal at 0 K is zero; this is a statement of the third law of thermodynamics
- see Figure 16.5
- the standard entropy values S^o of many common substances at 298 K and 1 atm are listed in Appendix 4
- because entropy is a state unction of the system (it is not pathway dependent), the entropy change for a given chemical reaction can be calculated by taking the difference between the standard entropy values of products and those of the reactants
- generally, the more complex the molecule, the higher is the standard entropy value

16.6 Free Energy and Chemical Reactions

- for chemical reactions often interested in the **standard free energy change**, the change in free energy that will occur if the reactants in their **standard states** are converted to the products in their standard states
  - note that the standard free energy change is not measured directly
- why is it useful to know) G^o for a reaction; knowing the) G^o values for several reaction allows us to compare the relative tendency of these reactions to occur; the more negative the value of) G^o, the further a reaction will go to the right to reach equilibrium
- the equation to use is) $G^o =$) $H^o - T$) S^o
- a *second method* for calculating) G for a reaction takes advantage of the fact that, like enthalpy, free energy is a state function; therefore can use procedures for finding) G that are similar to those for finding) H using Hess's law
- a *third method* for calculating the free energy change for a reaction used standard free energies of formation
- the standard free energy of formation () G^o_f) of a substance is defined as the change in free energy that accompanies the formation of 1 mole of that substance from its constituent elements with all reactants and products in their standard states

16.7 The Dependence of Free Energy on Pressure

- the equilibrium position of a process represents the lowest free energy value available to a particular reaction system
- the free energy of a reaction system changes as the reaction proceeds, because free energy is dependent on the pressure of a gas or on the concentration of species in solution
- will deal with only the pressure dependence of the free energy of an ideal gas; the dependence of free energy on concentration can be developed using similar reasoning
- see text for derivation
- $\Delta G = \Delta G^o + RT\ln(Q)$, where Q is the reaction quotient (from the law of mass action), T is the temperature (K), R is the gas constant, ΔG^o is the free energy change of for the reaction with all reactants and products at a pressure of 1 atm

The Meaning of Δ G for a Chemical Reaction

- a value of ΔG for a given reaction system tells us whether the products or reactants are favored under a given set of conditions, it does not mean that the system will proceed to pure products (if ΔG is negative) or remain as pure reactants (if ΔG is positive); instead, the system will spontaneously go to the equilibrium position, the lowest possible free energy available to it

16.8 Free Energy And Equilibrium

- from a thermodynamic point of view, the equilibrium point occurs at the lowest value of free energy available to the reaction system
- see Figure 16.8
- recall $\Delta G = \Delta G^o + RT\ln(Q)$, at equilibrium $\Delta G = 0$ and $Q = K$, then $\Delta G^o = -RT\ln K$
  - (1) when $\Delta G^o = 0$ the system is at equilibrium when the pressures of all reactants and products are 1 atm, which means that K equals 1
  - (2) when $\Delta G^o < 0$ means that $K > 1$; the reaction will adjust to the right to reach equilibrium
  - (3) when $\Delta G^o > 0$ means that $K < 1$; the reaction will adjust to the right to reach equilibrium
- see Table 16.6

16.9 Free Energy And Work

- achieving the maximum work available from a spontaneous process can only occur via a hypothetical pathway; any real pathway wastes energy
- see Figure 16.10